PARAMAGNETISM OF SINGLE CRYSTALS OF THE SALTS OF THE IRON GROUP OF ELEMENTS AT LOW TEMPERATURES. PART II. INVERSION OF THE STARK-PATTERNS FOR SIX-COORDINATED Ni^{++} AND Co^{++} IONS AND FOR FOUR AND SIX-COORDINATED Co^{++} IONS

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(*Received for publication, May 11, 1948*)

ABSTRACT. The present paper deals with the magnetic behaviour of the salts of the Co^{++} ion which is in the $^4F_{9/2}$-state. It is well known that though both the Ni^{++} and the Co^{++} ions have F-ground states, there is a fundmental difference in the magnetic behaviours of their salts having similar structures. It is a particularly striking achievement of the crystalline field theory of Van Vleck, Penney and Schlapp, Gorter and others that it gives a simple explanation of the behaviour of the salts of Ni^{++} and Co^{++}. It is shown (*a*) that *in a given field* the Stark-pattern of the ground state of the Co^{++} ion is inverted with respect to that of Ni^{++} ion; (*b*) that for octahedrally six-coordinated Ni^{++} salts the lowest lying state in the Stark-pattern is a singlet, whereas, for similar Co^{++} salts it is a triplet and (*c*) that as one passes from octahedral six-coordination to tetrahedral four-coordination the potential of the electric field at the central paramagnetic ion changes sign from positive to negative, which is equivalent to an inversion of the Stark-pattern. From this point of view it is evident that the six-coordinated cobalt salts studied here should show a complicated behaviour as against the simple behaviour of similar nickel salts dealt with in Part I of this paper. Further, the four-coordinated blue cobalt salt Cs_2CoCl_4 studied here should behave very similarly to the six-coordinated Ni^{++} salts. Temperature variation of the anisotropy and the effective moments of all these salts have been studied between 300 K and 80°K. The blue cobalt salt due to its similarity with nickel salts forms suitable material for calculating the spin-orbit coupling constant for Co^{++} ion, which agrees well with the spectroscopic value. The crystalline field constants for the blue cobalt salt have also been calculated and are found to be of nearly the same order of magnitude as in Ni^{++} salts and independent of temperature. The results for the six-coordinated cobalt salts serve to elucidate many of the obscure facts regarding the crystalline electric fields acting in these salts.

INTRODUCTION

In Part I of the present paper (Bose, 1948) we gave a general outline of the theory of the crystalline electric fields of Van Vleck (1932), Bethe (1932) and others and also some experimental results on the F-state ions Ni^{++} and Cr^{+++}, which are marked for their simplicity of behaviour and hence formed very suitable materials for a quantitative discussion on the merits of the theory. It was pointed out there, how even the nicer details of the theory, such as the small deviations from the Curie Law of the principal suscep-

TABLE I

For Principal Anisotropies of Crystals.

$Cs_2 Co Cl_4$ Orthorhombic, $a : b : c = 0.38 : 1.0.65$			$CoSO_4(NH_4)_2SO_4, 6H_2O$ Monoclinic, $\beta = 106°54'$ $a : b : c = 0.7392 : 1 : 0.498$				$CoSO_4K_2SO_4, 6H_2O$ Monoclinic $\beta = 104\ 54'$ $a\ b\ c = 0.7404 : 1 : 0.5037$				$CoBeF_4(NH_4)_2\ BeF_4, 6H_2O$ Monoclinic, $\beta = 106°46$ $a : b\ c = 0.740 : 1 : 0.485$			
(1) 'b' axis vertical, 'a' axis along the field (2) 'a' axis vertical, 'b' axis along the field			(1) 'b' axis vertical (2) '(001) plane horizontal, 'b' axis normal to field				(1) 'b' axis vertical (2) 'a' axis vertical, 'b' axis normal to field				(1) 'b' axis vertical (2) 'a' axis vertical, 'b' axis along the field			
Temp°K	$\chi_a - \chi_c$ $\times 10^6$	$\chi_b - \chi_b$ $\times 10^6$	Temp°K	Angle between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp°K	Angle between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp°K	Angle between 'a' axis & χ_1 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$
297.1	327.0	254.0	303.1	60	3023	1559	303.1	30.5	2532	1832	299.1	54.9	2930	1586
280	413.9	268.0	280	60	3604	1874	280	30.5	3005	2210	280	54.9	3324	2144
260	449.8	293.3	260	60	4204	2212	260	30.5	3478	2605	260	54.9	3809	2574
240	497.1	315.1	240	60	4922	2621	240	30	4038	3004	240	54.6	4402	3142
220	543.0	348.1	220	59.5	5791	3165	220	29.5	4709	3563	220	53.5	5140	3886
200	601.9	382.1	200	59	6880	3870	200	29	5521	4200	200	52.2	6053	4795
180	676.4	432.8	180	59	8241	4717	180	28.5	6563	5021	180	51.2	7216	6000
160	769.8	492.3	160	59	10080	5842	160	28.5	7863	6128	160	50.5	8690	7579
140	898.9	577.6	140	58.5	12600	7473	140	28.5	9638	7551	140	49.9	10830	9872
120	1090.0	704.1	120	58	15950	9572	120	28.5	12030	9334	120	48.9	13750	12850
100	1373.0	890.6	100	58	19960	12070	100	28.5	15240	11570	100	48.4	17210	15370
90	1580.0	1014.0	90	58	22150	13460	90	28.5	17080	12770	9	48.4	19250	18380
83.8	1760.0	1126.0	81.7	58	23380	14260	82.1	28.5	18580	13720	80.8	48.4	19930	19000

tibilities, the temperature variation of the anisotropies, the prediction of the strength of spin-orbit coupling, the great constancy of the crystalline electric fields and so on, were fully corroborated by our experimental results. The present paper deals with the Co^{++} ion which also is in an F-state and though the interpretation of the results here are less quantitative, they are none-the-less startling, as verifying one of the most interesting features of the electric field theory, namely, the fundamental difference in the behaviour of the Ni^{++} and Co^{++} ions, though both are in the F-state, as also that of the same Co^{++} ion but differently coordinated.

The mode of experimental procedure and the treatment of the experimental data have been already described in earlier papers (Bose, 1948) and it would be enough to tabulate here (Tables I and II) the final values of the principal anisotropies $\chi_1-\chi_2$ and $\chi_1-\chi_3$, the values of the principal gm. ionic susceptibilities χ_1, χ_2 and χ_3 corrected for diamagnetism, and the values for the principal and the mean effective moments p_1, p_2 and p_3 in terms of Bohr magnetons, all within the range of temperatures 300°K and 80°K. Figs. 1 to 4 are also given to follow these temperature variations more effectively.

TABLE II

For the gm. molecular principal susceptibilities and the squares of the effective magnetic moments (*Corrected for diamagnetism*).

Crystal	Crystal suspension and the direction along which the susceptibility is measured, *i.e.*, the direction setting along field	Temp °K	$\chi_1 \times 10^6$	$\chi_2 \times 10^6$	$\chi_3 \times 10^6$	p_1^2	p_2^2	p_3^2	p^2
Cs_2CoCl_4.	'*a*' axis vertical, '*b*' axis along field	296.8	8515	8373	8118	20.36	20.02	19.41	19.93
		182.7	13596	13355	12035	19.88	19.54	18.91	19.11
		83.8	29269	28635	27509	19.57	19.14	18.39	19.03
$CoSO_4(NH_4)_2SO_4, 6H_2O$	(20$\bar{1}$) plane vertical, '*b*' axis horizontal, normal to (20$\bar{1}$) plane along field*	296.0	11564	8370	9915	27.57	19.95	23.64	23.72
		185.2	19112	11238	14631	28.49	16.76	21.82	22.36
		84.7	42510	19130	28250	29.00	13.05	19.28	20.11
$CoSO_4K_2SO_4, 6H_2O$.	'*b*' axis vertical, 'χ_1' axis along field	296.6	11885	9218	9919	28.40	22.03	23.78	24.71
		171.1	20455	13347	14978	28.19	18.40	20.65	22.41
		82.4	40585	22085	26865	26.95	14.66	17.83	19.81
$CoBeF_4(NH_4)_2BeF_4, 6H_2O$	'*b*' axis vertical, 'χ_1' axis along field	296.7	11250	8262	9554	26.89	19.74	22.83	23.15
		185.8	18670	11822	13069	27.94	17.69	19.55	21.73
		86.8	39610	19680	20550	27.70	13.76	14.37	18.61

* Angle (001) : (20$\bar{1}$) = 64°48′

DISCUSSIONS

1. *The difference in the Stark-pattern of Ni^{++} and Co^{++} ions under the same type of electric field and its effect on their magnetic behaviours.*

If we consider the various ions of the iron group in which the number of electrons, n, in the $3d$ shell, increases progressively from 0 to 10, the spin quantum number S, as is well known from Hund's rule, is equal to $n/2$ in the first half of the group and to $(10-n)/2$ in the second half, *i.e.*, the spin quantum number increases from 0 to 5/2 and then diminishes, reaching 0 at $n=10$. On the other hand, the orbital quantum number L of the ion has zero values not only for $n=0$ and $n=10$, but also for $n=5$ as can be seen from the table below.

TABLE III

No. of $3d$ electrons- n	0	1	2	3	4	5	6	7	8	9	10
Ground state	$^1S_0$	$^2D_{3/2}$	$^3F_2$	$^4F_{3/2}$	$^5D_0$	$^6S_{5/2}$	$^5D_4$	$^4F_{9/2}$	$^3F_4$	$^2D_{5/2}$	$^1S_0$
Ions	K^+, V^{+5}	Sc^{++}, Ti^{+3}, V^{+4}	Ti^{++}, V^{+3}.	V^{++}, Cr^{+3}, Mn^{+4}.	Cr^{++} Mn^{+3}.	Mn^{++} Fe^{+3}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Cu^+ Ca^{++}

It is assumed as before that with the crystalline electric fields involved in the *ionic salts* of these ions the coupling between L and S is broken down but not those between the different l's that compound into L or the different s's that compound into S. As is well known, under such circumstances the effect of the electric field will be to give rise to a Stark-splitting of the ground state of the ion corresponding to a complete or partial removal of the $(2L+1)$-fold orbital degeneracy of the ion without much affecting the spin degeneracy, which latter will be completely removed only on the application of a magnetic field. The degree of removal of degeneracy and in consequence the nature of Stark-pattern will evidently depend upon how strong and asymmetric the electric fields are.

For the usual type of the ionic salts of the iron group, the most simple yet satisfactory electric field is one of which the potential is expressed by

$$V=Ax^2+By^2-(A+B)z^2+D(x^4+y^4+z^4) \qquad \ldots \quad (1)$$

where the fourth power terms represent a predominant cubic field on which is super-imposed a small rhombic field represented by the squared terms. Under such a crystalline field an F-state will, in general, split up into a Stark-pattern consisting of a singlet and two adjacent triplets, each level of which will, in general, suffer a partial removal of the spin degeneracy corresponding to the effect of the spin-orbit coupling and to the second order

Kramers splitting, except when the number of electrons in the incomplete 3d shell is odd, so that a two-fold Kramers spin degeneracy will be always left over. The separation due to the cubic field will be very large, of the order of 10^4 cm^{-1}, compared to the rhombic separation.

It has been shown by Van Vleck (1932) that in the Stark-pattern for the F-state ion under the above type of electric field, since the singlet level must always lie on one side, it may either correspond to the highest or the lowest value of the energy in the pattern. Which it is will be decided by the sign of the cubic field constant D, in the expression (1). If the singlet level is lowermost, since the triplets will be far removed from it, cubic separation being of the order of 10^4 cm^{-1}, practically the singlet level alone will be occupied at all ordinary temperatures.* Since this level retains almost all its $(2S+1)$-fold spin degeneracy in the crystalline field, the ion will behave very nearly like S-state ions, in having a feeble anisotropy, a nearly spin only value of the effective moment, and a small deviation from Curie Law. On the other hand when the triplet level is lowermost, the separation between the components of the triplet, being produced by the feeble rhombic field, will be comparable to kT, and the population of the *upper components of the lowest level* will be quite appreciable. The magnetic behaviour in such a case will therefore evidently be much more complicated.

In the ionic salts of the iron group of elements, the electric fields in the neighbourhood of the paramagnetic ion may arise either due to a distribution of four equal negatively charged ions at the corners of a tetrahedron, or due to six equal negative charges at the corners of an octahedron. Güter (1932) has shown that the sign of D, the cubic field constant in the expression (1) for the potential due to these charges, is negative in the first case and positive in the second. An X-ray examination of the disposition of the negatively charged atoms round the paramagnetic ion will therefore serve to decide uniquely the sign of D.

In the iron group of elements, where the number of electrons n in the $3d$ shell increases from 0 to 10 from the beginning to the end of the group, any atom or ion with $n=x\leqq 5$, will have the same orbital quantum number L, as one for which $n=5-x$ or $5+x$ or $10-x$, (Van Vleck, 1932). Hence, in a given cubic field, *i.e.*, with the sign and the value of D determined, all of the ions will have exactly the same Stark-pattern, except for the fact that the patterns for some of the ions will be inverted with respect to those of the others, and knowing the Stark-pattern for one, those for the others may be uniquely determined. If we regard the pattern for $n=x$ as erect, then the pattern for $n=5+x$, will also be erect, whereas the patterns for $n=5-x$ and

* In the final considerations, however, the populations of the upper levels cannot be neglected and the contribution of these levels to the total magnetization, which is quite appreciable, will come through the so called temperature independent "high frequency" terms.

$10-x$ will be inverted. For example, if we regard the pattern for Cr^{+++} with $n=x=3$, erect for a given sign of D, the pattern for Ni^{++} with $n=8$, will also be erect, but those for Ti^{++} with $n=2$, and Co^{++} with $n=7$, will be inverted. Though it does not seem possible to decide from *a priori* considerations, whether in a cubic field with positive D, say, an F-state ion like Cr^{+++} will have its singlet level lowermost or uppermost, still it is possible to make this decision from other considerations; for example, from the magnetic behaviour of salts in which the distribution of the negative charges around the Cr^{+++} ion is known from X-ray data and hence the sign of D. In all the Tutton salts and in the hydrated sulphates, selenates, oxalates, etc., the distribution is known from X-ray data to be of the octahedral type, and hence D should be positive in these salts. The characteristics found in the magnetic properties of Cr^{+++} salts of this type, namely, the close conformity to the spin only value and to the Curie Law, and the low magnetic anisotropy, even when the crystal is not cubic, show that in these salts the singlet level should be the lowermost in the Stark-pattern of Cr^{+++}. *If we agree to call the Stark-pattern of the F-state ions erect when the singlet level is lowermost*, then we can conclude from the magnetic data for Cr^{+++}, that in a cubic field with positive D, the pattern for Cr^{+++} should be erect; from which using the inversion rule deduced above, we conclude that in the same field the pattern should be erect for Ni^{++} as well, but inverted for Co^{++} salts. The magnetic properties of both Ni^{++} and Co^{++} salts of the above type do confirm this conclusion.

2. *Simple magnetic behaviour of four coordinated ionic Co^{++} salts as related to the inversion of the Stark-patterns.*

Now, since a change in the sign of D, from positive to negative or *vice versa*, will produce an inversion of the pattern (Van Vleck, 1932) we may conclude that when D has a negative sign, as will be the case when the distribution of the negative charges is tetrahedral, the pattern for Co^{++} will become erect, whereas the patterns for Cr^{+++} and Ni^{++} will be inverted. No four-coordinated ionic salts of trivalent chromium are known and the four-coordinated salts of Ni^{++} that are known are found to be square-coordinated and covalently, and are therefore diamagnetic. Ionic salts of Co^{++}, however, are available in which a tetrahedral four-coordination is known to occur, *e.g.*, the blue double chlorides Cs_2CoCl_4 and Cs_3CoCl_5. The structures of these two crystals have been analysed by X-ray methods by Powell and Wells (1935) and they find that each cobalt ion is surrounded by four negatively charged chlorine atoms, which occupy the corners of a tetrahedron, with the Co^{++} ion at the centre. Both these salts have been studied magnetically at room temperature by Krishnan and Mukherji (1938) and are found to have a much feebler anisotropy, about 4 to 6%, and the effective magnetic moments are much closer to

the 'spin only' value, than in the ordinary cobalt salts in which the Co^{++} ion is six-coordinated.

We have studied the temperature variation from room temperature down to 80°K, of the anisotropies and of the principal susceptibilities of one of them, namely, Cs_2CoCl_4 which is ortho-rhombic. The results obtained can be discussed in relation to the splitting of the energy levels in the crystalline field in the same manner as in octahedrally coordinated Ni^{++} and Cr^{+++} salts (Bose, 1948), to which the double chlorides of cobalt are analogous. The values of the three field constants α's for this crystal, calculated from the magnetic data, are given in the following table .—

TABLE IV

For the values of the crystal field constants α_a, α_b and α_c for Cs_2CoCl_4

Temperature °K	$-\alpha_a \times 10^6$	$-\alpha_b \times 10^6$	$-\alpha_c \times 10^6$
296.8	200.7	191.1	174.0
182.7	205.7	195.5	177.8
83.8	211.3	200.8	182.2

It is remarkable that the α's are of nearly the same magnitude as in six-coordinated Ni^{++} salts (*loc. cit.*). Here again the α-values remain unaffected by changes of temperature, as is to be expected.

The effective magnetic moment along the χ_a axis say, will be given by the expression,

$$p_a^2 = p_o^2\left[1 - 3kT\alpha_a + 8\lambda\alpha_a + \frac{\Delta_a\lambda^2}{kT}\right] \qquad \ldots (2)$$

which, using the values of α above and the spectroscopic value of λ for $Co^{++} = -180\ cm^{-1}$, becomes

$$\left.\begin{aligned} &= 15(1 + .1280 + .2966 + .0040) = 21.43 \\ \text{and similarly, we have} \\ p_b^2 &= 15(1 + .1217 + .2819 + .0008) = 21.07 \\ p_c^2 &= 15(1 + .1106 + .2564 - .0048) = 20.43 \end{aligned}\right\} \qquad \ldots (3)$$

all at room temperature 297°K. The relative importance of the terms is thus roughly the same as for the six-coordinated nickel salts. The theoretically calculated values for the magnetic moments agree with the experimental values which are shown in Table II and Fig. 1. Here again as in nickel one can, using the measurements of the magnetic anisotropies at different temperatures, calculate the constant of the spin-orbit coupling λ, which agrees with the spectroscopic value of λ given above, as is evident from the data in Table V. These data further corroborate the already mentioned fact that the crystal field constants remain practically independent of temperature.

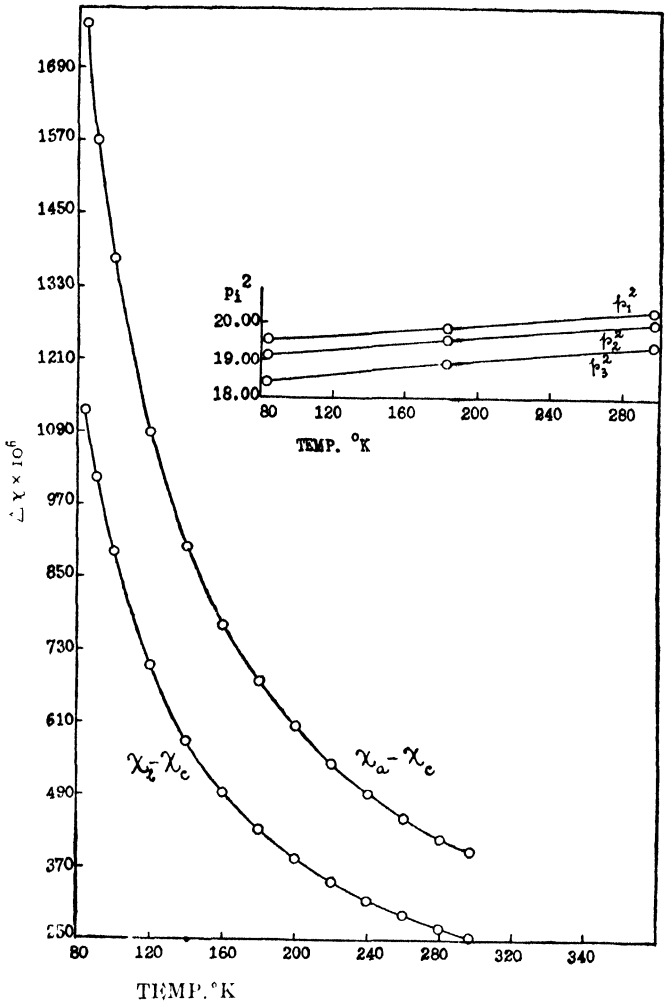

FIG. 1

Temperature variation of principal anisotropies and effective moments: Cs_2CoCl_4

TABLE V

For values of the ratio of $\Delta\chi$ at temperatures T to that at room temperature (297.1°K)

Temperature°K.	λ = — ·0 cm⁻¹, Ratio obtained from		
	Calculation	$\chi_a-\chi$ Obs	$\chi_b-\chi_c$: Obs.
297.1	1.000	1.000	1.000
265	1.140	1.133	1.113
200	1.500	1.516	1.501
160	1.933	1.939	1.938
100	3.504	3.159	3.506
83.8	4.172	4.433	1.433

3. *Complicated behaviour of the six-coordinated Cobalt salts.*

In the ordinary salts of cobalt like the hydrated sulphates, selenates, etc. in which the Co^{++} ion is octahedrally six-coordinated, the cubic field constant D will be positive, unlike in the blue cobalt salts considered previously and hence the singlet level will be the uppermost, whereas, the triplet level the lowermost in the Stark-pattern of the Co^{++} ion in the former crystals. With such a disposition of the Stark-pattern in which the lowermost level is a triplet, whose components have been separated to extents comparable with kT, by the rhombic part of the field, and the spin degeneracy of each component also slightly removed through the spin-orbit coupling, the calculation of the principal susceptibilities in terms of the crystalline field constants becomes complicated and laborious.

An approximate calculation, however, has been made by Penney and Schlapp (1932) on the simplifying assumption that $B=0$ in the expression (1), so that $C=-A$, and further that D_q the cubic field constant used by Penney and Schlapp instead of D, is $\sim 1200\ cm^{-1}$; nearly the same as in the nickel salts having similar coordination. They have made these calculations of the principal susceptibilities for two limiting cases for which $A=40$ corresponding to a small value of rhombic field and $A=200$, a very high rhombic field. For the first value, all the squares of the three principal moments p_1^2, p_2^2, p_3^2 are found to fall with lowering of temperature, slowly at first and rapidly at low temperatures. For the second value, p_2^2 and p_3^2 are found to diminish as before, whereas, p_1^2 rises slowly at first but rapidly at lower temperatures, reaching a maximum at very low temperatures. The theoretical curves for p_1^2, p_2^2, p_3^2, obtained by them for these two rhombic fields are given in their paper referred to above and are reproduced here in Figs. 5 and 6.

Experimentally, Bartlett's measurements (1932) on the principal susceptibilities of cobalt ammonium sulphate from $+50°C$, to $-25°C$, show a small rise in p_1^2, with lowering of temperature and appear to conform to the latter-field in this respect rather than to the former. On the other hand, there are serious diffculties, as pointed out by Penney and Schlapp, in accepting such a high rhombic field, as it leads to too high an anisotropy and too low values for the effective moments to fit with Bartlett's experimental results. For these and other considerations Penney and Schlapp are in favour of an intermediate value of the rhombic field, closer to the first than to the second.

Our present measurements extend to much lower temperatures than Bartlett's. They confirm the small increase in the p_1^2 values by Bartlett in cobalt ammonium sulphate, and a similar rise is observed also in cobalt ammonium fluoberyllate. In the crystal of cobalt potassium sulphate, however, the value shows a small fall instead of a rise (See Figs. 2 to 4).

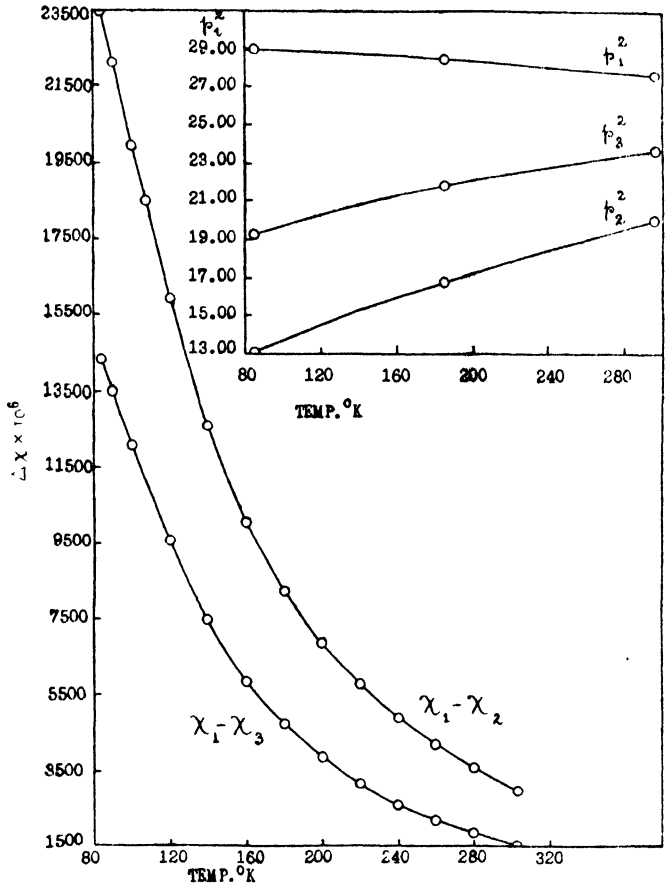

FIG. 2

Temperature variation of principal anisotropies and effective moments : $Co(NH_4)_2(SO_4)_2, 6H_2O$

Since the crystalline fields in all the three crystals should be more or less similar, one should not attach too much importance to the small rise in the p_1^2 values in the two ammonium salts, in making the choice of the rhombic part of the field. Apart from the difficulties pointed out by Penney and Schlapp in choosing a high rhombic field, our low temperature values for the three principal magnetic moments rule out the high rhombic field altogether. Even a casual examination of the experimental results compared with the theoretical values will convince one of this. To emphasise the point we are giving below the experimental values for p_1^2, p_2^2 and p_3^2 at 80°K for comparison with the theoretical values calculated from the two fields. The observed values fit fairly closely with the lower rhombic field and in any case completely rule out the higher field.

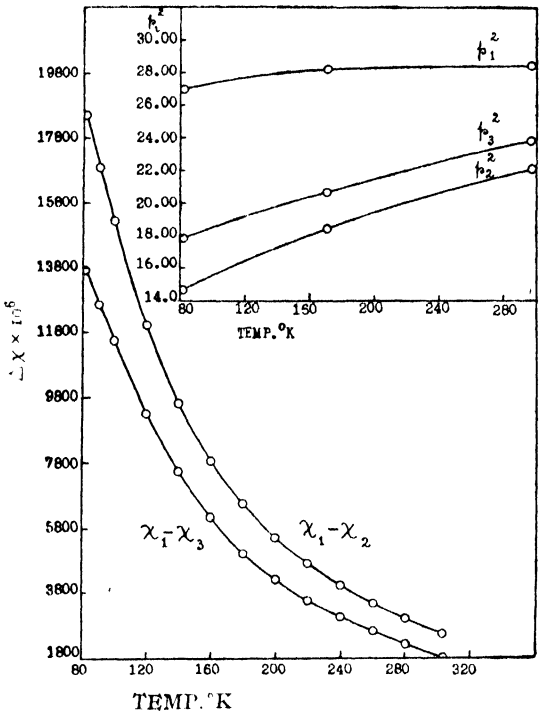

FIG. 3

Temperature variation of principal anisotropies and effective moments: $CoK_2(SO_4)_2, 6H_2O$

TABLE VI

For observed and calculated values of p_1^2, p_2^2 and p_3^2 at 80°K

Squares of principal moments		p_1^2	p_2^2	p_3^2
Observed	$CoSO_4(NH_4)_2SO_4, 6H_2O$	29.1	12.9	19.1
	$CoSO_4K_2SO_4, 6H_2O$	26.0	11.5	17.7
	$CoBeF_4(NH_4)_2BeF_4, 6H_2O$	27.9	13.1	13.9
Calculated	A = 40.	28.2	10.7	17.0
	A = 200.	41.0	1.8	16.6

We have further evidence in support of this choice from the measurements made by Jackson (1924) on the magnetic anisotropies of cobalt ammonium sulphate, which extend down to 14°K. The magnetic data as given by Jackson are however so improbable that Penney and Schlapp have been forced to reject them altogether. Since then, however, an error has been found in Jackson's calculation by Krishnan, Chakravorty and Banerji, (1933). On correcting for this error it is found that in the temperature range overlapping ours the values for the principal magnetic moments for cobalt ammonium sulphate agree very well with our own, and hence we may presume that at lower temperatures also, the recalculated values of Jackson are more or less correct, The values of p_1^2, p_2^2 and p_3^2 for cobalt ammonium sulphate,

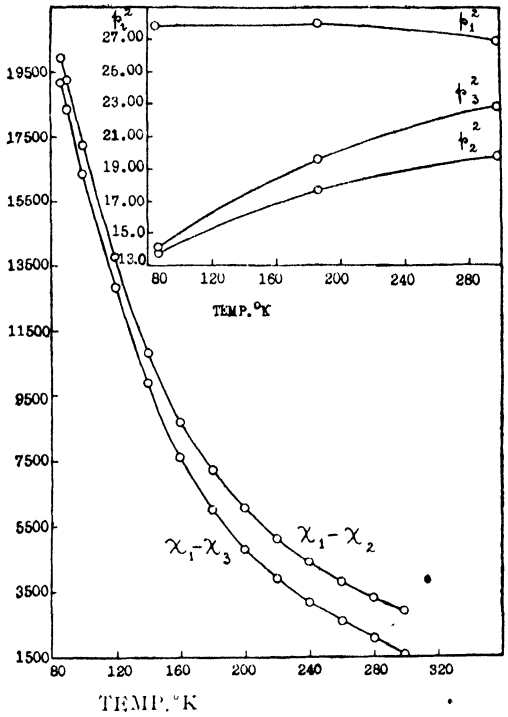

FIG. 4

Temperature variation of principal anisotropies and effective moments $Co(NH_4)_2(BeF_4)_2, 6H_2O$

TABLE VII

For effective magnetic moments of $CoSO_4(NH_4)_2SO_4, 6H_2O$ at different temperatures by different workers.

Author	Temp°K	p_1^2	p_2^2	p_3^2
Bartlett	328	28.19	21.37	25.13
	293	29.06	20.77	25.35
	276		—	25.20
	269.5	29.29	20.19	—
	262	—	—	25.14
	253	29.72	20.19	25.37
Jackson	290	26.88	19.72	22.92
	77.2	27.71	11.65	18.84
	20.3	23.90	8.311	14.63
	16.7	24.00	7.508	14.31
	14.5	23.45	7.276	13.91
Present Author	296.0	27.57	19.95	23.64
	185.2	28.49	16.76	21.82
	84.7	29.00	13.05	19.28

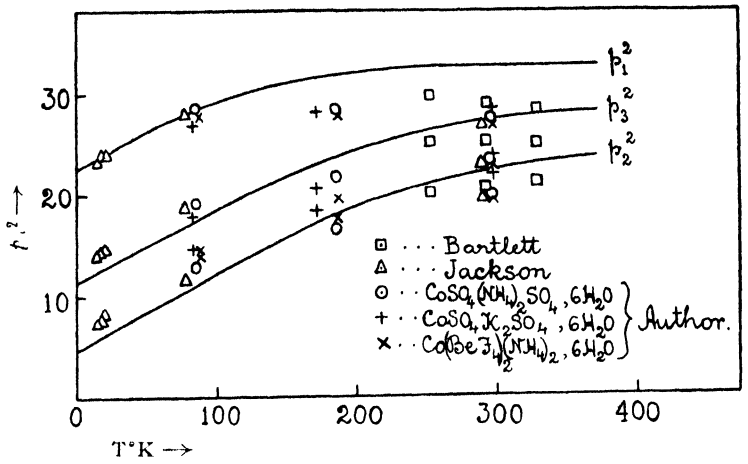

FIG. 5
Rhombic field small, A = 40

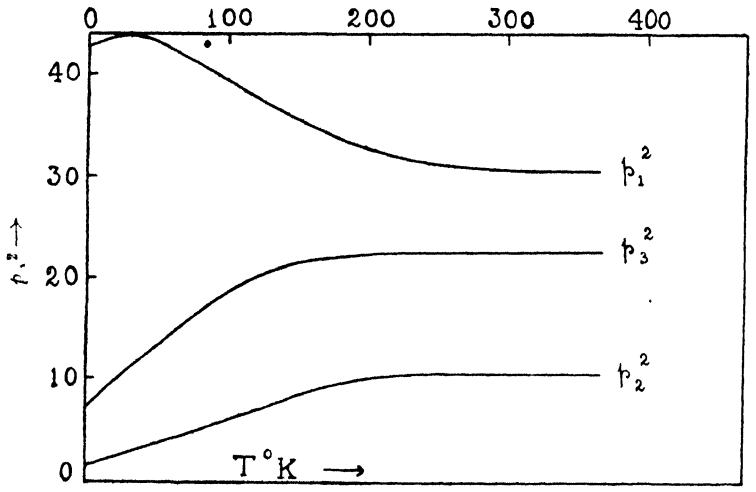

FIG. 6
Rhombic field large, A = 200

recalculated from Jackson's data, along with Bartlett's and author's data are given in Table VII and are further plotted in Fig. 5 for comparison. They agree well in the temperature ranges where they overlap. Thus Jackson's low temperature values also rule out completely the higher rhombic field and are in favour of the lower field.

Even when the most suitable value of A, has been selected, it is not to be expected, however, that the agreement between the theoretical and the experimental values will be close, when we remember that in Co^{++} the influence of the rhombic part of the field is very large. There are two reasons for this.

The choice of the rhombic field for discussion (Penney and Schlapp, *loc. cit.*) was guided by considerations of simplicity in calculation. The expressions for the principal susceptibilities besides depending on D_q,

involves in a complicated manner the two rhombic field constants $\sigma=\frac{1}{2}(A+B)$ and $\delta=\frac{1}{2}(A-B)$. Special choice by Penney and Schlapp of these constants amount to $\sigma=\delta=20$ or 100, for the two limiting cases discussed above. These discussions may be regarded as merely demonstrating that σ and δ are of the order of 20. Any attempt at a closer fit with experimental data should aim now at finding the proper value of σ and δ *separately*, rather than find values for $\sigma=\delta$ other than 20, which would give a better fit, since no value of σ, if it is to be taken as equal to δ, can be expected to give a close fit.

There is another reason and a strong one, which would make even such attempts futile with our present incomplete knowledge of the fine structure of these crystals. The theoretical calculations were made on the tacit assumption that the electric field axes, associated separately with all the ions in the unit cell, are respectively parallel to each other, which is not generally true. The Tutton salts of cobalt contain two Co^{++} ions in the unit cell and are monoclinic, the principal axes of one of the ions thus being the mirror reflections of those of the other ion, in the (010) plane. Denoting the principal magnetic moments of the *ion* by P_1, P_2, P_3 respectively, to distinguish them from principal moments for the *crystal* p_1, p_2, p_3 it can be readily seen that

$$\left.\begin{aligned} p_1^2 &= P_1^2\alpha_1^2 + P_2^2\beta_1^2 + P_3^2\gamma_1^2 \\ p_2^2 &= P_1^2\alpha_2^2 + P_2^2\beta_2^2 + P_3^2\gamma_2^2 \\ p_3^2 &= P_1^2\alpha_3^2 + P_2^2\beta_3^2 + P_3^2\gamma_3^2 \end{aligned}\right\} \quad \ldots \quad (1)$$

where $\alpha_1, \alpha_2, \alpha_3$, are the direction cosines of P_1 ; $\beta_1, \beta_2, \beta_3$ of P_2 ; and $\gamma_1, \gamma_2, \gamma_3$ of P_3 respectively, with reference to the p_1, p_2, p_3 axes for the *crystal* as a whole. The theoretical calculations of Penney and Schlapp refer to P_1^2, P_2^2 and P_3^2 which, as will be seen from the expression given above, are not the same as p_1^2, p_2^2 and p_3^2 respectively. Unless we know the direction cosines defining the orientations of the three field axes associated with one of the paramagnetic *ions* in the unit cell, with reference to the three principal axes associated with the *crystal*, *i.e.*, in the absence of a detailed knowledge of the dispositions of the atoms surrounding the two paramagnetic ions, we cannot calculate the P's from the observed p's and hence cannot attempt the calculation of the field constants A and B.

These considerations thus also supply an explanation of the variation of the magnetic behaviour from crystal to crystal of the cobalt salts as observed experimentally (see Table II) ; since even if the field in the neighbourhood of the paramagnetic ions, which determines the P's are exactly the same in all the three crystals—not only as regards the cubic part but also the rhombic part—the relative orientations of the two paramagnetic groups in the unit cell may not be the same in the different crystals. Conversely, the observed fact that p_1^2 curves of the three cobalt salts differ from one another slightly, or the p_2^2 curves or the p_3^2 curves, should not be regarded as necessarily indicating a difference in the crystalline fields in the three crystals.

Though it is tempting to do so, such an explanation would be trivial, since we know definitely that the α's, β's and γ's should vary from crystal to crystal, as evidenced by the χ_1 direction being different in the three salts. The variation of the α's, β's and γ's alone should be sufficient to produce all the observed differences in the curves for p_1^2 or p_2^2 or p_3^2 of these salts, since, the temperature variations of P_1^2, P_2^2 and P_3^2 for the cobalt ion in a given field are so different from one another.

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